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D21H 19/52 *(2006.01)*

(54) **Composition for paper deacidification, process to obtain it and method for its application**

Zusammensetzung zur Papierentsäuerung, Verfahren zum Erhalten davon und Verfahren zu ihrer Anwendung

Composition de désacidification de papier, procédé permettant de l'obtenir et son procédé d'application

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EP-A1- 1 132 431
WO-A1-2005/083176
US-A- 3 676 182
US-A1- 2009 148 575

EP 2 626 464 B1

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Description

Backgroung of the invention

[0001] The present invention relates to a new chemical composition based on a suspension of hydroxyapatite nanoparticles (HAp) in carboxymethyl-cellulose (CMC) in alcoholic solution (isopropylic alcohol), used for paper deacidification, by acidity anihilation from 4.5 to 7.2. There are shown the composition preparation, the process to obtain it and method for its application.

State of the art

[0002] The paper degradation, due to an excessive acidity (due to chemical or biological action), is reflected by the yellow tonalities appearance accompanied by an increased brittlement of the paper, which is transformed into a very fragile substance that is destroyed at the slightest touch. The acid hydrolysis of cellulose that occurs during aging, represents about 95% of the paper damages, and is considered as the most significant cause of deterioration of cellulosic materials. Acid attack causes a random attack on hemi-acetal bonds between different constituents of cellulose molecules. This reaction will weaken the molecules, leading to the brittlement of cellulosic materials.

[0003] The most frequently encountered paper damages are:

- Increased acidity (due to either pollutants or inks used to print) which led to a decreased mechanical strenght until the holes appearance. This is accompanied by the erosion and brittlement, thinning, making them transparent.
- Staining appearance of brown, yellowish, green, pink, purple, orange spots, accompanied by a deeper unvisible degradation, due to different fungi and in particular, due to some pigments produced by them;
- "foxing: or the appearance of some redheads-brownish spots of 0.5-5 mm diameter, due to the fungi, and in particular due to the cessation of their action. These foxing spots may be produced by the moulds, too, which generally live unnoticed in the paper, and become visible by their smell and by the brown color marked upon paper permeability.

[0004] The processes employed to remove paper acidity are known as paper deacidification purposes. In spite of the investigations carried out so far, the issue of the paper deacidification is far from being resolved. Some methods of mass deacidification purposes have been developed and improved, but nevertheless no one can say that any of them meet fully the criteria of featured quality in the field, such as pre-selection of the material to be restored, drying, duration of treatment, the effect of the inks, color, paper covers, acidity neutralization, final pH, alkaline reservoir, risks to the restorer and reader, the impact on the environment, the cost of the equipment and the cost of treatment.

[0005] Up to now, the main discoveries in the field are:

D1. The patent EP 1 132 431 A1 (MITSUI CHEMICALS INC [JP], presents the use of an aqueous solution of polymer particles with carboxyl group, as carboxymethyl cellulose, carboxymethyl starch, carboxymethyl chitin, and propyleneglycol alginate, mixed with inorganic fine particles (calcium phosphate or tricalcium phosphate), easily soluble in water, with a diameter of 500 nm or less, in a proportion of 10: 90 or 99: 0.01 (mass report) and in solvents such as: water, methanol, ethanol, isopropanol, acetone, ethylene glycol, propylene glycol. The invention shows the use of hydroxyapatite, fluoroapatite, chloroapatite, apatite, carbonate-containg apatite, magnesium-containing apatite, iron-containing apatite, and tricalcium phosphate for achieving a more transparent film-components with composition above 0.01%-20%, preferably 0.1-10% percentages. This material is applied by conventional means, such as: impregnation, a size press, a gate roll coating, a calander, a blade coater and spraying.
The drying temperature varies between 100-180 °C, this temperature being considered too high for a manuscript or an old book with fragile paper. In addition, the authors employs a method consisting in the application on the sheet of paper some polymeric films based on polyvinyl alcohol, polyvinyl metacrylamide and pyrrolidone, all of them having carboxyl groups grafted on their structure.
By comparison with this invention, our invention is using a new composite, based on HAp:CMC 50-50% (mass ratio) in solvent isopropanol (non-toxic and friendly environmental solvent), the method of application being spraying, drying being performed in the air, without additional sources of heat, cooling or lighting.

D2. U.S. patent 0148575, A1/2009**,** presents a method of paper producing of a stable paper, used for food packaging, containing a layer printed with an ink containing a fluorescent dye, a polimeric material containing a microincapsulated material for a latent heat storage, in a solvent or mixture of solvents (ethanol, 1-propanol and 2-propanol, ethyl acetate, isopropyl acetate, etc., or mixtures thereof). The microcapsules are produced in the presence of at least a protector colloid which can be neutral or anionic compound of inorganic nature (metal salts, salts, oxides and hydroxides of magnesium, calcium, iron, zinc, nickel, titanium, aluminium, silicon, barium, manganese and aluminium, hydroxyapatite, bentonite and hydrotalcite) or organic (hydroxyethyl acrylate, methyl cellulose, hydroxyethylcellulose, methylcellulose and carboxymethyl cellulose, and also polyvinyl

pyrrolidone, copolymers of vinylpyrrolidone, gelatine, Arabica gumm, xanthan, sodium alginate, caseine, polyethylene glycol, preferably PVA, or partially hidrolized polyvinyl acetates and methyl hydroxypropilcellulose). They are used as spray agents, facilitating spray drying, with free-flow or improved redispersion properties, and used as thickeners. However, the method does not provide informations on the stability in time of the treated paper and the implications on the quality of the paper and of products packed in it. In addition, the application of some fluorescent dyes, can lead to an acceleration of the degradative processes of paper (through photochemical reactions of their chromophores groups), and in some cases, due to the importance of historical manuscripts, some of which may not be covered with coloured films which could cover the written information.

D3. US patent 3 676 182/1972**,** presents a treatment method for the printed cellulosic materials (books or manuscripts), based on a process of nonaqueous deacidification purposes and preservation of cellulosic materials, by using a solution of alkali alkoxides or earth alkaline alkoxides (such as methoxyde, ethoxyde or propoxyde of magnesium), or a mixture of both, in an organic solvent (chlorinated hydrocarbonated derivatives and/or fluorurated). As a result of this treatment, the paper may even increase alkalinity to pH 11. This method has the major disadvantage of using alkoxides, particularly toxic organic compounds, both for the manuscript, as well as for user restorer. In the same context is the method of Wei t'O, which leads to good results for deacidification purposes, but does not provide a long-term uniformity of alkaline reserve; due to its low solubilities of the reagents in methanol, they produce side effects on inks. In addition, the use of magnesium isopropyl carbonate isopropoxyde as agent for deacidification purposes, and some freons as cooling agents, some negative effects on paper, on the environment and on restorer, are observed. As a result, the acids from the paper are neutralised through the formation of magnesium sulphate and magnesium carbonate deposit which act as buffer, pH 7-8. Alkaline reserve created in paper from this process is relatively slow and nonhomogeneous, so that after a short time it is necessary to repeating the deacidification process.

D4. Patent WO 2005\/083176 A1**,** refers to a process of preserving cellulosic material by using a stabilizing agent (which may be a deacidification agent, such as: alkaline earth metals derivatives, hidrocabonated fluorurated or chlorinated derivatives, a chlorinated solvent C1-C4 (propanol) and a cooling process in a temperature range between -50 °C to 0 ° C, preferably -20 ° C ÷ -5 °C, and varing the refrigeration operations (storage room, stabilising agent or cellulosic material).

D5. In the German Patent DE19921616 (A1**),** it is used a neutralizing method of the acidity of historical paper using a dispersion of calcium carbonate or magnesium carbonate (1.2% mass percent) with organic acid as stabilizer in cyclohexane. But, this method uses an organic solvent (cyclohexane, with a high degree of flammability and toxicity) existing the ignition danger of the material (book) during the treatment. In addition, the treated material is hardly drying and can assign on some certain foxing area.

D6. Patent US2005042380 (A1**),** entitled: Basic suspension, preparation and deacidification process of the paper, which dealt with basic type suspensions, Li_2O Na_2O, K_2O, MgO, CaO, SnO, SnO_2, PbO, Pb_2O, Pb_2O_3, PbO, BiO, Bi_2O_3, Sb_20_3 or their mixtures, as well as hydroxides with sizes ranging from 10 nm to 500 nm and paper deacidification by materials imersion into some bath with suspensions of oxides and bases above-mentioned. This method has the side effect of cellulose depolimerization, due to strong alkaline conditions. In the same context are the patents AU2003215817 **and** WO03082742**,** where are shown only the synthesis methods of these nanoparticles, mentioning their potential application in the above mentioned area. **In the paper entitled; "Conservation and restoration of records and books'** authors: Carmen Crespo and Vicente Vinas, addressed a number of restoration methods of deteriorated papers, including the application of calcium hydroxide and magnesium hydroxide in solution, barbotating of carbon dioxide, on the paper surface so a layer of carbonate of the two metals above mentioned could be formed. The method has as drawbacks:

- formation of carbonate in the form of solid nonuniformly distributed and easily exfoliated on the paper surface;
- the use of carbon dioxide, which can lead to the formation of carbonic acid, which would increase the acidity of treated paper with stronger destructive effects on this paper.
- The generated carbonates could cover the used pigments belonging to figures or drawings from the paper and could produce lightening, making harder the color reviving.

Very similarly, the publication: Nanoparticules of Mg $(OH)_2$: Synthesis and applications in conservation of paper, authors: Giorgi, R., Bozzi, C., Dei Gabbiani, C., Ninham, B. W., Baglioni, P. Langmuir 21, 8495-8501 (2005), some alternative preparation methods of $Mg(OH)_2$ and the reagents effect on the

quality of this hydroxide is shown; its use in the deacidification of some paper samples by transforming it into the corresponding carbonate on the paper surface, is presented, too.

The paper "A new method for deacidification of paper-based on calcium hydroxide dispersed in aqueous environments," authors: Giorgi, R., Dei, Schettino, L., Baglioni, P, published in Preprint of the IIC Baltimore Congress 2002, Work of Art on Paper, Books, Documents and Photographs: Techniques and Conservation, 69, Baltimore (2002) where the application of calcium hydroxide in suspension, is shown. Unfortunately, calcium hydroxide, magnesium hydroxide, barium hydroxide in aqueous solutions, intense used in the last decade, induce undesirable side effects due to the strong alkaline conditions which causes cellulose depolimerization subsequently the treatment. In addition, for paper samples with alkaline reservoir, which have undergone the deacidification process, atmospheric CO_2, weak acid, is causing a pH decreasing of the solutions used for deacidification purposes with more than 1.5 pH units. It contributes to a mild dissolution of alkaline-earth inorganic metals carbonates present in the system.

D7. In the book "Preservation technologies of books", the U.S. Congress, Office of the promotion of technology, Washington, D. C., there are presented some problems and their solutions for some books. An additional reliable process, from Preservation Technologies, Inc., used MgO with particles sizes between 0.1 and 0.9 microns, a surfactant and perfluoroheptan as solvent (toxic and undesired solvent due to the interdictions imposed by the environmental agencies concerning the use of freons).

D8. The U.S. patent 5091111 **and** U.S. Patent 5208072**,** deals with a composition for paper deacidification containing 0.1-20% methyl magnesium carbonate in an organic solvent which does not attack the paper, but requires special precautions due to its toxicity. Organic compounds are used in the patent U.S. 5770148, too, by refeering to an improved deacidification method, for the paper printed books and other printed material containing cellulose, by treating the material with metallic basic oxides, hydroxides or salts dispersed in hidrofluoreter, alone or in combination with perfluorinated transporters, in presence of surfactants.

D9. US patent 6676856 presents improvements to the composition and method for preservation of cellulosic materials by using metal organic carbonates solutions, alcohols C_1-C_4, with a moisture content of less than 100 ppm, and 86-99% solvent with a moisture content of less than 100 ppm.

D10. **The patent:** RO126570 (A2**) entitled:** Composition and process for treatment, chemical restoration and biological disinfection of historical paper surface with hydroxyapatite nanoparticles, it is presented the preparation and application of a suspension of hydroxyapatite nanoparticles in isopropylicalcohol, in a concentration of 0.08 ... 0.8% for chemical restoration and biological desinfection (for Aspergillus **Ş**i Penicillium fungi) for the surface of a deteriorated paper.

Disclosure of the invention

[0006] Regarding to the State of the art presented and exemplified the above-mentioned part, analyzing the advantages and disavantages of the methods and compositions featured in State of the art, it appears necessary that a new composition avoiding the application of: polymeric dispersion containing carboxilated polymers and inorganic particles (D1, D2); their composites with various inorganic particles (D1, D2), toxic solvents and neprieteno**Ş**i environment (D3, D7, D8) and of the compounds which after application support the carbonatation losing the alkaline reserve of paper (D5, D6, D7, D8).

[0007] In comparison with all these inventions, the present invention is to provide a new method for paper safeguard and conservation, by using nanosized hydroxyapatite (30 nm), mixed with carboxymethyl cellulose (the last compound being a compound with similar structure with the structure of the paper) in isopropanol solvent (solvent environment friendly and non-toxic), and prevent the destruction or impairment of the recognized printed or printed paper.

Detailed description of the invention

[0008] For this invention was used hydroxyapatite (HA) in the form of nanoparticles prepared by grinding of a hidroxyapatite powder in a vibrator vessel, until it has reached a size of about 30 nm. In order to avoid lowering alkali reservoir of the paper supporting deacidification, Hap, in the form of nano-powder was mixed with a solution of carboxymethyl-cellulose (CMC) in isopropylic alcohol 50%: 50% (percentage by weight), and the obtained suspension is applied on the surface of the acid attack damaged paper.

[0009] By using carboxymethyl-cellulose (CMC), a super activation of hidroxyapatite (HAp) is intended by strengthening of electrostatic and hydrogen bonding between the two components, in order to get a smoothing paper surfaces where it is applied this suspension. Generally, HAp has hydrogen atoms bound to oxygen atom. On the other hand, the functional groups that contain pairs of positive charged ions of calcium and clusters of six atoms of oxygen negative charge associated with phosphate crystal triplets, generating hexagonal crystals with a columnar shape with Ca: P = 1.67. The ions Ca,

P and hydroxyl groups, are located on the HA surface. At the contact with CMC takes place an electrostatic attraction between Ca^{2+} ions from HAp with the carboxyl anions, from the CMC structure, which is not a classical ionic exchange interaction, being more intense in an acidic medium [Bernardi, G. Hydroxyapatite Chromatography of proteins, Methods Enzymol 22, 32-339 (1971)]. This means that, in the acidic environment of degraded paper, the two components will form a compact powder between them and with the paper support.

[0010] In our invention, the two components of the composition HAp: CMC at the primary contact, are interacting only by weak hydrogen bonds.The interaction between CMC with HAp in this composition is visible in FTIR spectra through the widening of OH group bands (3500-3000 cm^{-1}). By laying this composition on the paper with high acidity (pH 4.5), the electrostatic binding of the two components will be favored, too, forasmuch due to acidic pH, Ca^{2+} ions located on the surface of HAp come into contact with the $-COO^{2-}$ anions from the CMC surface. The electrostatic link between these two components is stabilizing and neutralizing the paper pH where it is sprayed (visible at 1460 cm^{-1} band of the FTIR spectrum, attributed to ionic pair $-Ca^{2+}COO^{2-}$). For this reason, the atmospheric CO_2 has the ability to react with none of these two components, the risk of transformation of pH paper from the basic range to acidic one, is practically null.

[0011] Novelty and advantages of the invention consist in:

- the use of hydroxyapatite nanoparticles suspension $Ca_{10}(PO_4)_6(OH)_2$ in carboxymethyl cellulose (CMC) in alcoholic solution (isopropylic alcohol) 50%: 50% (percentage by weight), the solution being sprayed on the acidic paper surface;
- layering on paper involves the hydrogen bonds between the H atoms and OH groups existing in the structures of the two components, as well as electrostatic binding of the two components favoured by acidic medium of the paper (pH 4.5), because in the field of the acidic pH, Ca^{2+} ions located on the HAp surface are coming into contact with the COO^{2-} ions from the CMC surface, forming ion-pairs $COO^{2-}Ca^{2+}$. For this reason, the atmospheric CO_2 has the ability to react with none of these two components, the risk of transformation of pH paper from the basic range to acidic one, is practically null.
- isopropylicalcohol has a low toxicity, it is volatile, has a low surface tension and is environment friendly. In addition, for books and other printed material, this solvent meets the requirements for solvents in such applications: not dissolve pigments, inks and adhesives from cellulosic materials.

[0012] In comparison with existing methods up to this point and used in many book deposits and libraries, the composition hidroxyapatite: carboxymethyl cellulose prepared by us, has the following advantages:

- (1) the nanoparticules of HAp and CMC are not toxic, being recognized as biocompatibile materials;
- (2) has minor disadvantages in terms of used solvent: Wei t 'O method is using CFC (freon);
- (4) the paper treatment with nanoparticles is not followed by carbonatation of the applied reagents, and there is no risk for the disappearance of paper alkaline reservoir and the reappearance of paper acidity.

[0013] Further, this invention is described in figures 1-5:

Figure 1 present FTIR spectra for indidual components of this composition with hydrogen bonds evidence (a) and the evidence of $COO^{2-}Ca^{2+}$ bond (b)

Figure 2, shows micrograms obtained by scanning electron microscopy (SEM) and atomic force microscopy (AFM) of untreated paper samples (left side a,b) and the samples of paper sprayed with HA: CMC 50% - 50% (isopropylic alcohol) (right side a,b);

Figure 3 shows the AFM topology of untreated acid paper;

Figure 4 shows the AFM topology paper after treatment with HAp: CMC = 50%: 50% in isopropylic alcohol

Figure 5 presents the visual evidence of an acidic paper samples before (left) and after treatment (right) with HAp: CMC = 50%: 50% in isopropylic alcohol.

[0014] There follows an example of the invention.

Example 1. Operations have been carried out by the treatment of a yellowed, lightened and brittled paper sample:

1. Removing the dust by a mechanical operation that was made with a soft brush, poor ventilation in the fume hoods;
2. Treatment of smoothing by mechanical tools with a soft brush and a bone palette knife;
3. Mechanical cleaning: dry powder gum and eraser;
4. Removing the dry wax with a scalpel;
5. 0.2 g HAp nano-powder was mixed with 100 ml isopropylicalcohol containing 0.2 grams carboxymethyl cellulose (CMC) 50%: 50% (percentage by weight), and the obtained suspension is applied by a spray on the surface of a deteriorated paper. The spraying suspension HAp: CMC has been applied by rotating movements in successive circles from left to right and

from top to bottom;
6. the paper in question is left to dry in the air at room temperature, so that to achieve new bonds between sprayed nanoparticles with cellulose fibers from the paper, in order to make the paper more consistent and strength. Drying will occur 24 hours at room temperature.
7. After the application of uniform flow of HAp-CMC in isopropylicalcohol, and drying, the paper was the subject of physico-chemical investigations, such as: FTIR, scanning electron microscopy (SEM) and atomic force microscopy (AFM). On the one hand, it could be observed, the topology of HAp nanoparticle in CMC suspension, their size and homogeneity of the HAp:CMC sample sprayed on paper, on the other hand.
8. The efficiency of presented composition in this invention is determined by pH measurements, too. For pH measurement, weighing 0.5 grams of not printed paper, subjected to ultrasonication defibrilation (for 15-20 minutes) with a special ultrasonicator in sealed tubes. After defibrilation, the pH has been measured continuously to a constant value. The measurements were carried out in triplicate. For the determination of the pH was used a pH-meter with a calibrated glass electrode. If at the primary contact between the paper and composition, the pH paper was 4.5, after treatment, its pH became 7.2.

[0015] It was stable for several years without any visual changes of treated papers. The treated paper was effectively deacidified without ink smearing over notes or text of the treated manscrisului / book.

Claims

1. A composition that consists of: hydroxyapatite and carboxymethyl cellulose (50%-50%) in 100 ml isopropylic alcohol.

2. A process for obtaining a composition according to claim 1 **characterized in that** it consists in the following stages: producing the suspension of carboxymethyl cellulose in isopropylic alcohol, producing hydroxyapatite nanoparticles, combining components obtained in the following proportions: 0,2g HA CMC, 100 ml isopropylic alcohol by shaking them vigorously,

3. Use of a composition according to claim 1 for paper deacidification, which comprises the following stages: removing the dust, mechanical smoothing by mechanical tools, mechanical cleaning, removing of deposits of dry wax, and applying such composition by spraying on the surface of the damaged paper, inducing the paper deacidification, with annihilating the paper acidity from pH 4,5 to alkaline mange pH=7,2 followed by drying for 24 hours at room temperature.

Patentansprüche

1. Zusammensetzung besteht aus: Hydroxyapatit und Carboxymethyl cellulose (50% - 50%) in 100 ml Isopropylalkohol.

2. Verfahren zur Herstellung einer Zusammensetzung erhalten nach Anspruch 1, damit gekennzeichnet, dass es in die folgenden Phasen besteht: der Suspension von Carboxymethyl cellulose in Isopropylalkohol Herstellung, Hydroxyapatit Herstellung von Nanopartikeln, die Kombination in Anteilen erhaltenen Komponente: 0,2 g HA CMC, 100 ml Isopropylalkohol, indem sie kräftig geschüttelt wird.

3. Verwendung der Zusammensetzung nach Anspruch 1 für Papierentsäuerung, die die Schritte umfasst: Entfernen der Staub, mechanischen Glättung durch mechanische Werkzeuge, mechanische Reinigung, trockenem Wachs zu entfernen und Zusammensetzung Auftragen von auf der Oberfläche Sprühen von das beschädigte Papier, das Papier Entsäuerung zu induzieren, mit der Papier Säure zu alkalischen Bereich von pH 4,5 bis pH 7,2 folgte trocknen von 24 Stunden bei Raumtemperatur getrocknet.

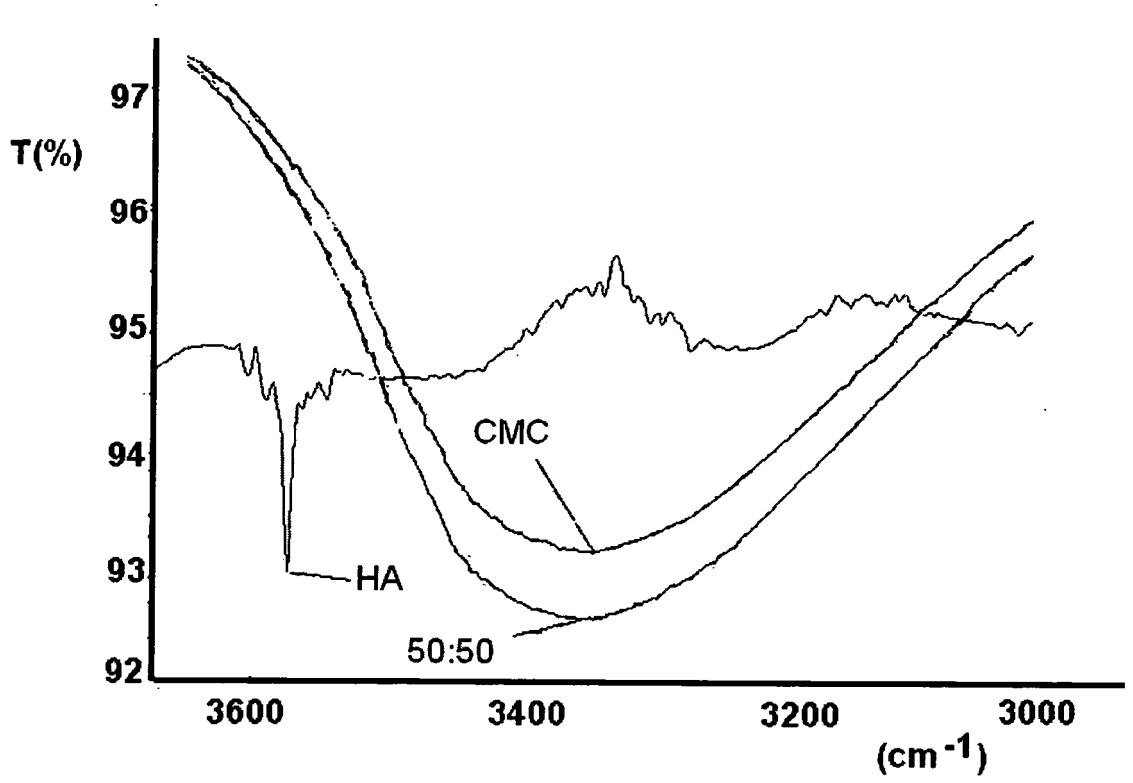
Revendications

1. Une composition constituée par: hydroxyapatite et carboxyméthyl cellulose (50% - 50%) dans 100 ml d'alcool Isopropylique.

2. Une procédé d'obtenir d'une composition selon la revendication 1 **caractérisé en ce qu'**il consiste à les étapes suivantes: la production d'une suspension du carboxyméthyl cellulose dans l'alcool isopropylique, la production des nanoparticules d'hydroxyapatite, combinant les components obtenus dans les proportions suivantes: 0,2 g de HA CMC, 100 ml d'alcool isopropylique en agitant vigoureusement.

3. Utilisation de la composition selon la revendication 1, pour la désacidification de papier, comprenant les étapes consistant à: enlever la poussière, le polissage avec des dispositifs mécaniques, nettoyage mécanique, l'enlèvement des dépôts de cire sèche, et en appliquant du cette composition par la pulvérisation sur la surface du papier endommagée, ce qui induit la désacidification de papier, en annihilation de l'acidité du papier à partir d'une pH 4,5 jusqu'a

le domaine alcalin pH = 7,2, puis séchage pendant 24 heures à température ambiante.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93
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HA
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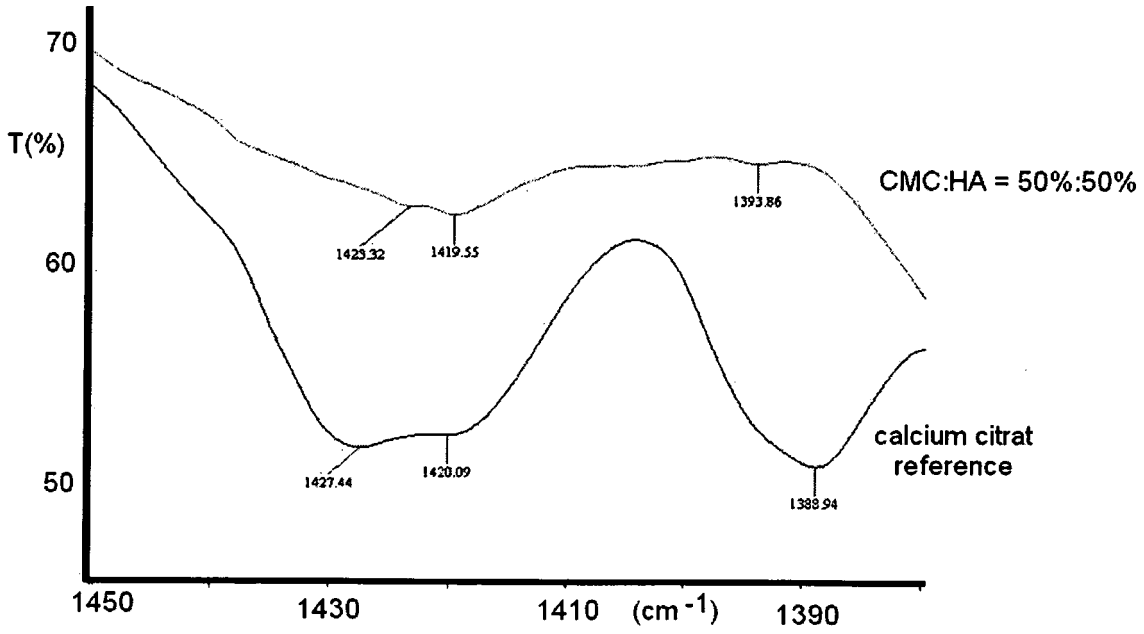
3400
3200
3000
(cm-1)

(a)


70
T(%)
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50
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1419.55
1393.86
CMC:HA = 50%:50%
1427.44
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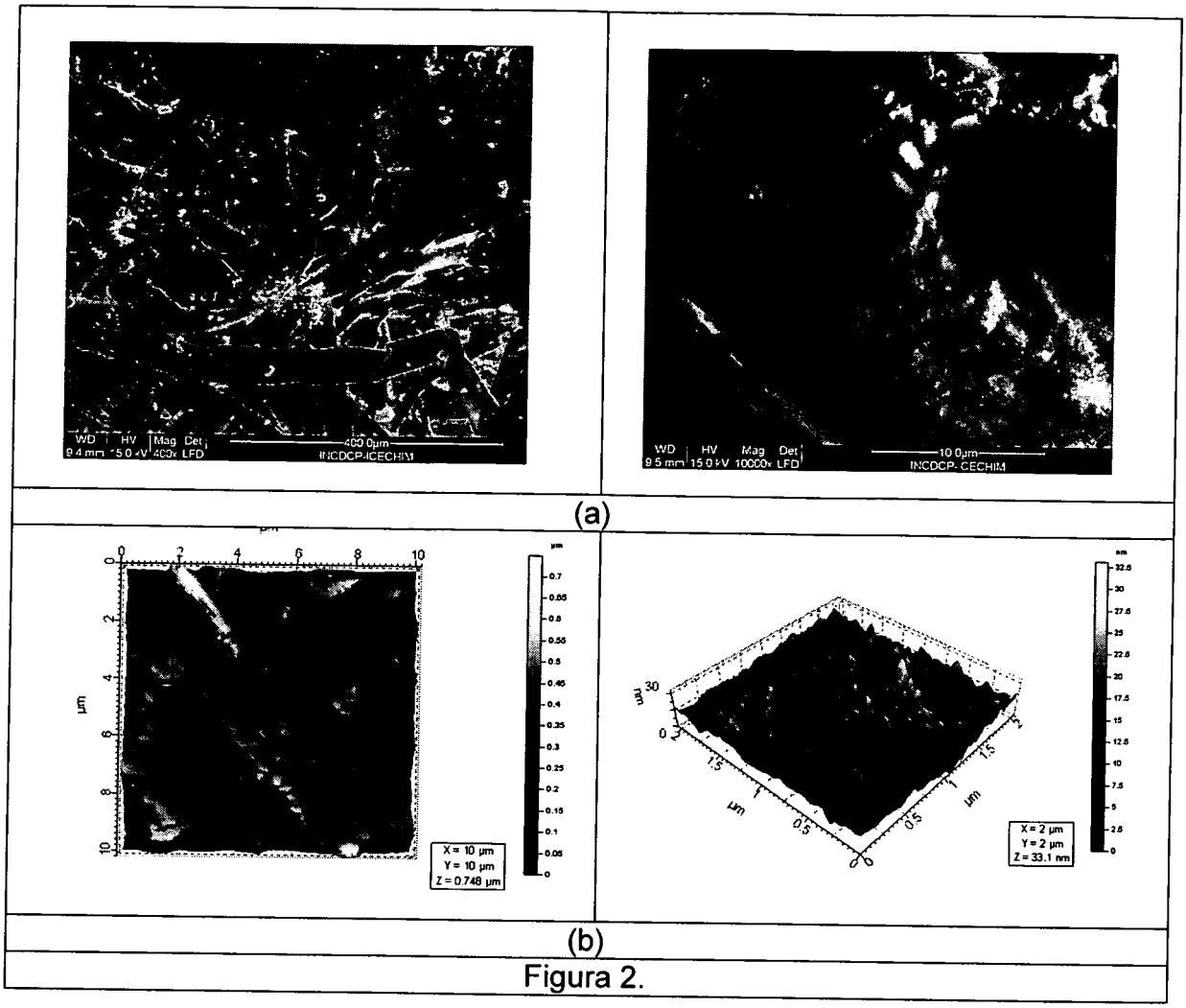
calcium citrat
reference
1450
1430
1410
(cm-1)
1390

(b)

Figure 1.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INCDCP-ICECHIM
WD HV Mag Det
9.5 mm 15.0 kV 10000x LFD
10.0µm
INCDCP- CECHIM
(a)
µm
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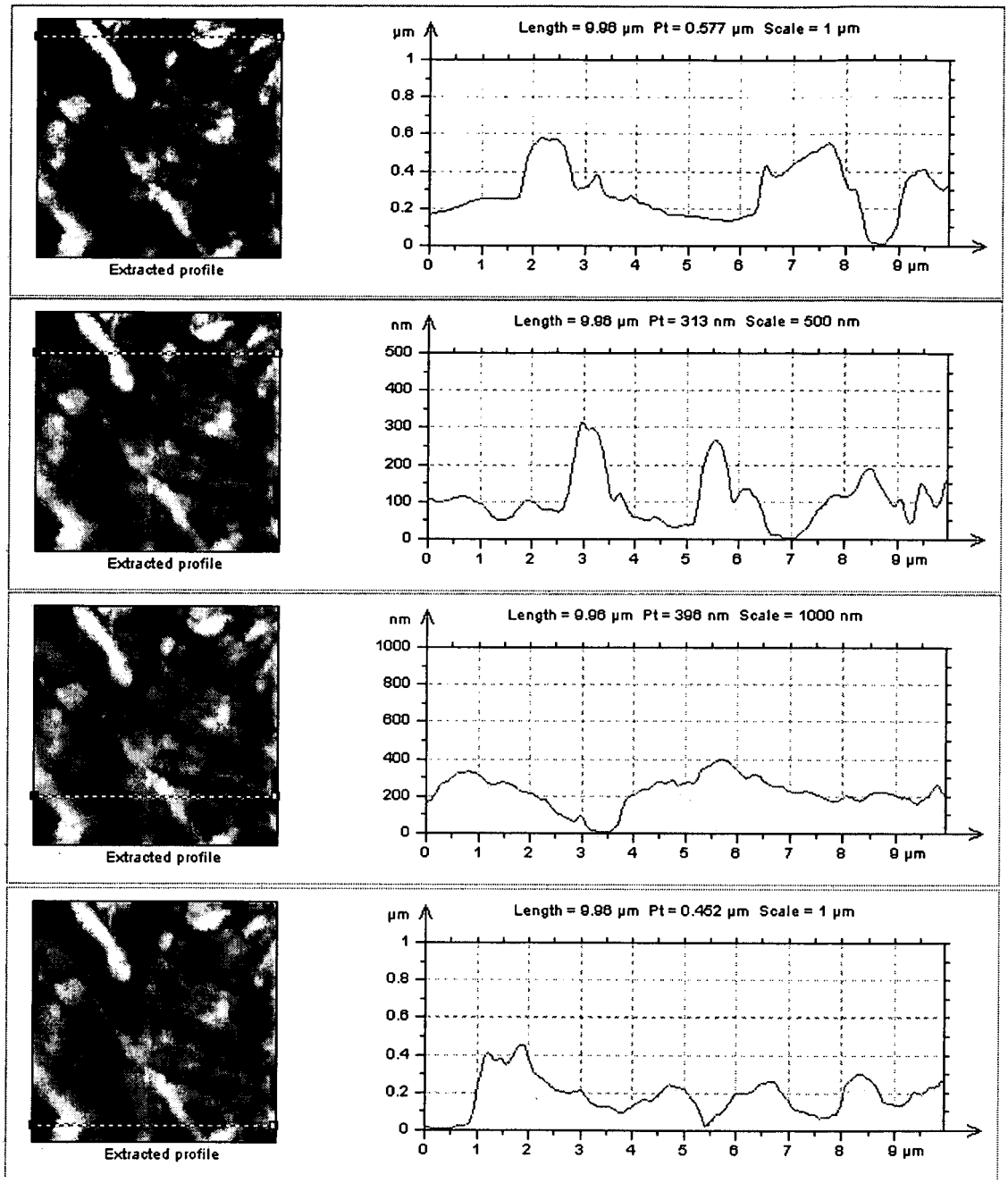
Y = 10 µm
Z = 0.748 µm
nm
X = 2 µm
Y = 2 µm
Z = 33.1 nm
(b)

Figura 2.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0.6
0.4
0.2
0
0 1 2 3 4 5 6 7 8 9 µm
Extracted profile
nm
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500
400
300
200
100
0
0 1 2 3 4 5 6 7 8 9 µm
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1000
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600
400
200
0
0 1 2 3 4 5 6 7 8 9 µm
Extracted profile
µm
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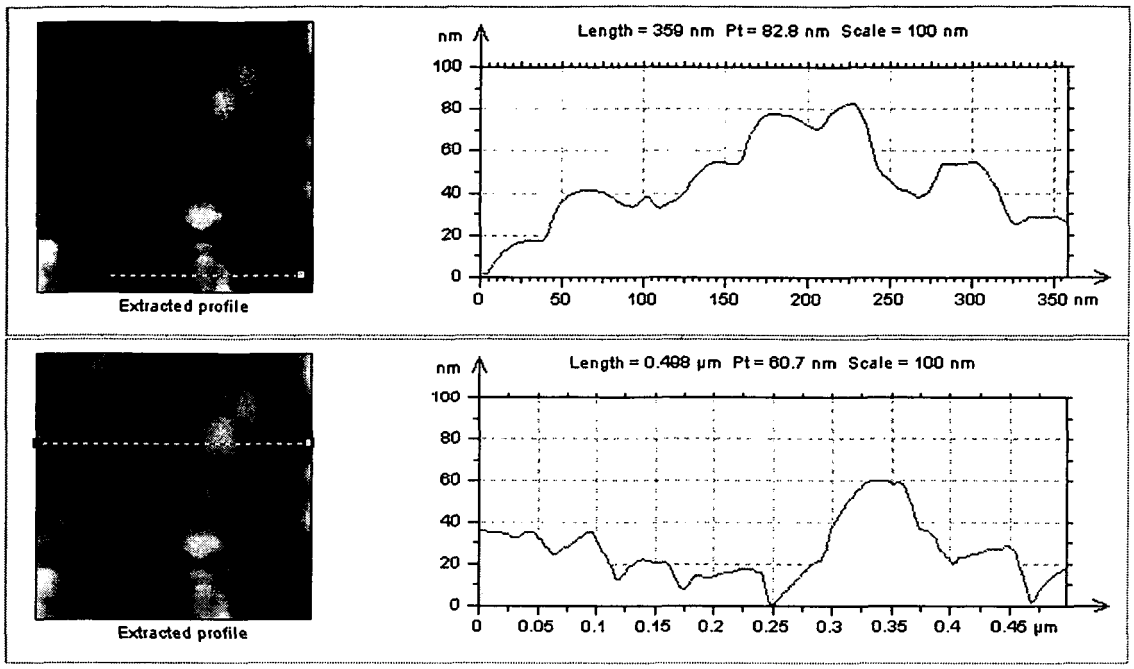
0.4
0.2
0
0 1 2 3 4 5 6 7 8 9 µm

Figure 3.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100
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200
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Extracted profile
nm
Length = 0.498 µm Pt = 60.7 nm Scale = 100 nm
100
80
60
40
20
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0.15
0.2
0.25
0.3
0.35
0.4
0.45 µm

Figure 4.

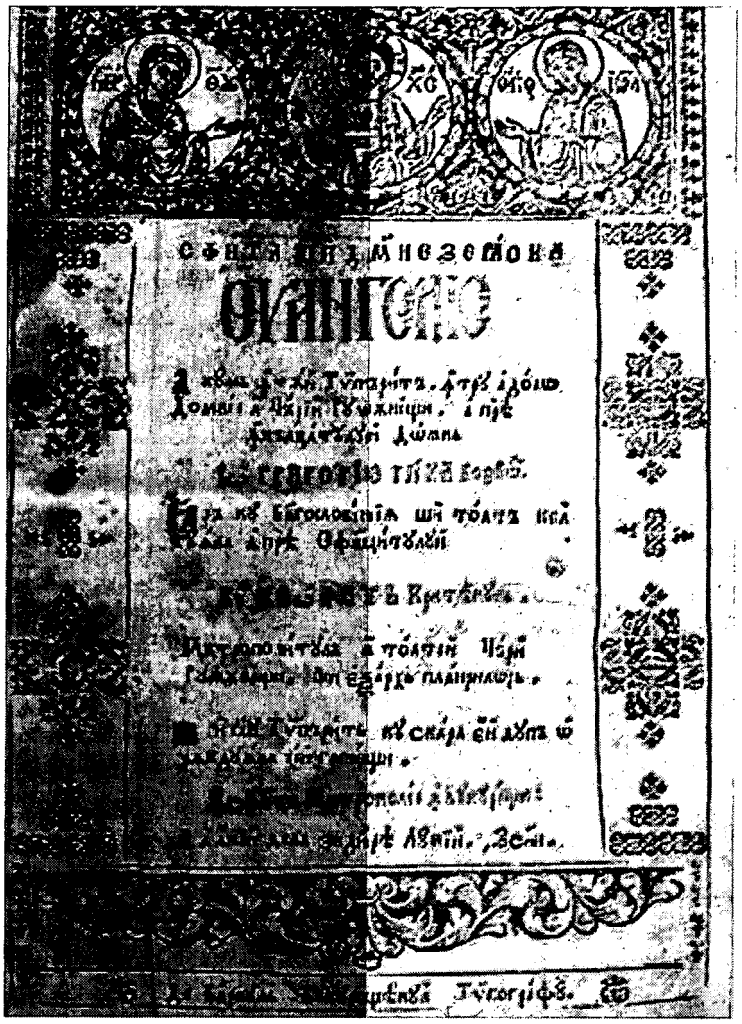

Figure 5.

REFERENCES CITED IN THE DESCRIPTION

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